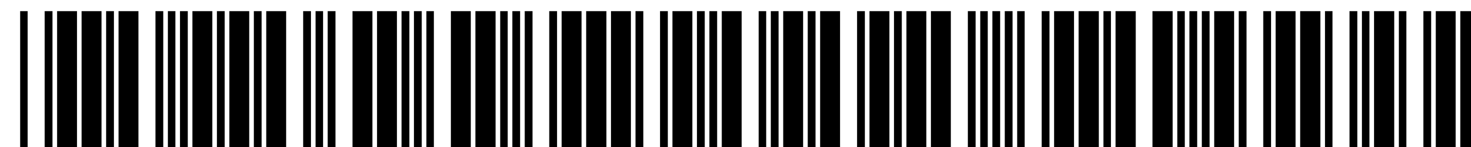
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(54) **METHODS OF FORMING ZINC OXIDE BASED II-VI COMPOUND SEMICONDUCTOR LAYERS WITH SHALLOW ACCEPTOR CONDUCTIVITIES**

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H01L 21/00 (2006.01)

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See application file for complete search history.

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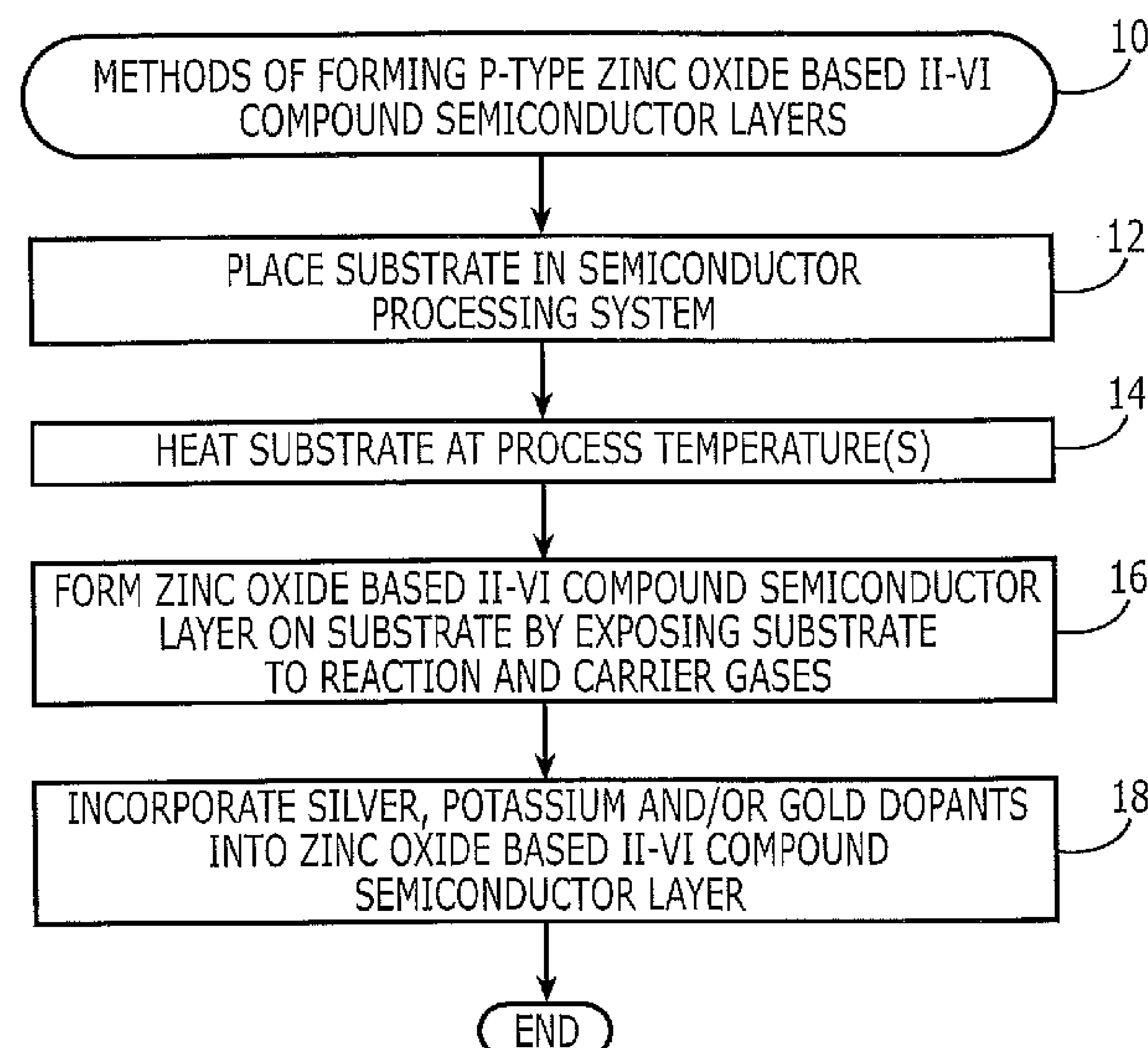
(57) **ABSTRACT**

A p-type ZnO-based II-VI compound semiconductor layer has silver, potassium and/or gold dopants therein at a net p-type dopant concentration of greater than about 1×10^{17} cm^{-3}. A method of forming the layer includes using an atomic layer deposition (ALD) technique. This technique includes exposing a substrate to a combination of gases: a first reaction gas containing zinc at a concentration that is repeatedly transitioned between at least two concentration levels during a processing time interval, a second reaction gas containing oxygen and a p-type dopant gas containing at least one p-type dopant species selected from a group consisting of silver, potassium and gold. A concentration of oxygen in the second reaction gas may also be repeatedly transitioned between at least two concentration levels. The concentration of zinc in the first reaction gas and the concentration of oxygen in the second reaction gas may be transitioned in an alternating sequence, so that relatively high zinc concentrations in the first reaction gas overlap with relatively low oxygen concentrations in the second reaction gas and vice versa.

11 Claims, 4 Drawing Sheets



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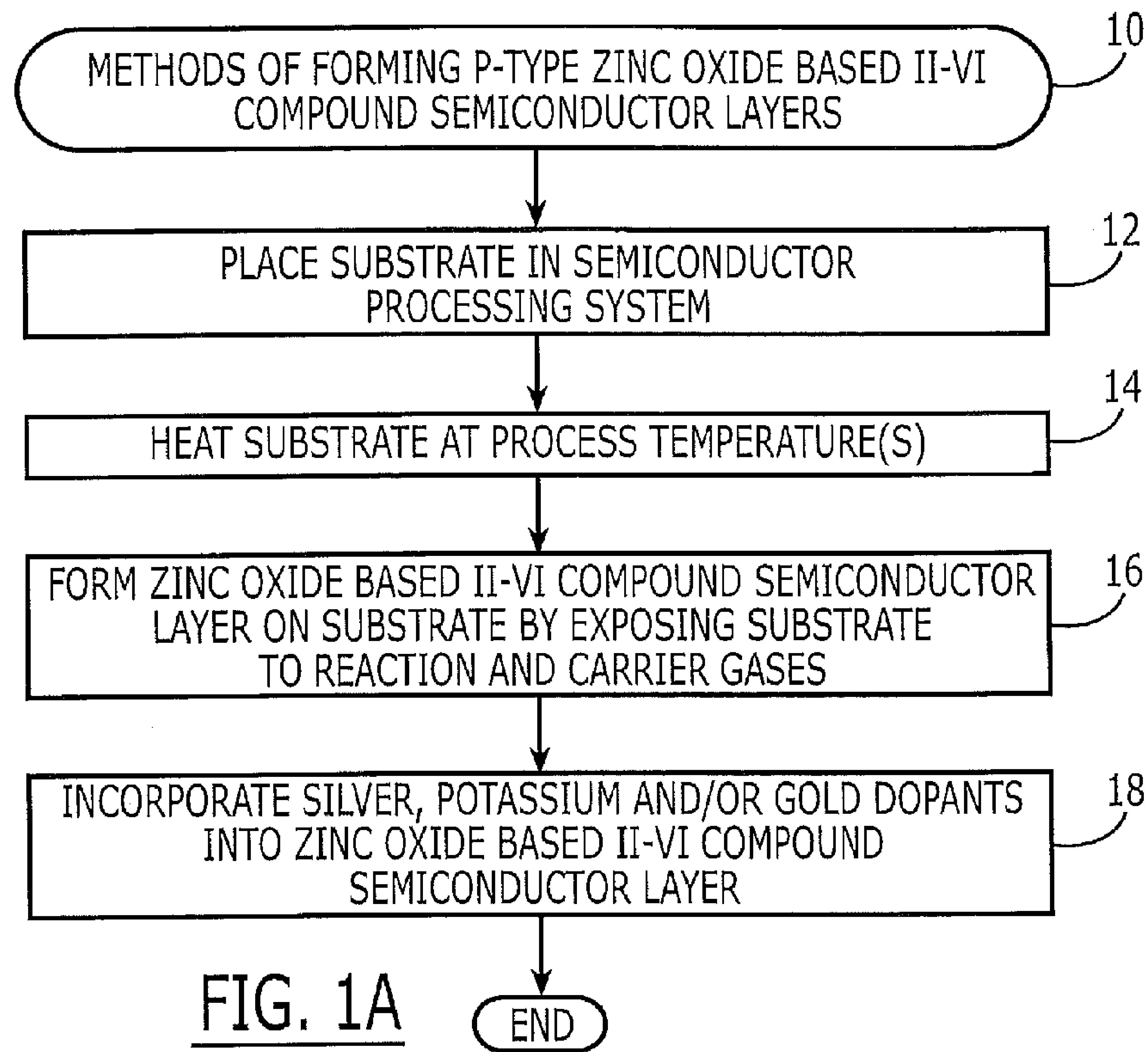

FIG. 1A

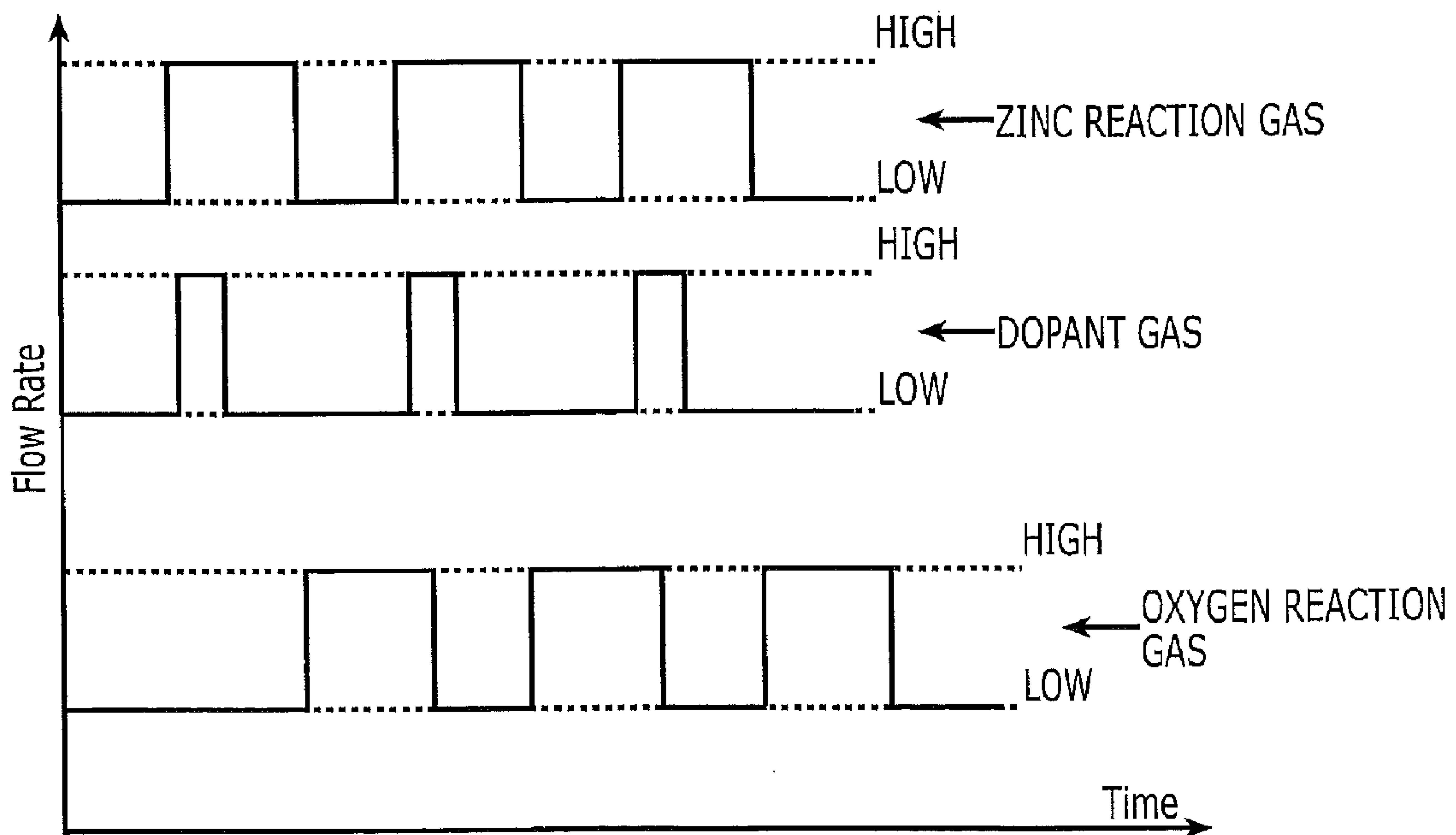

FIG. 1B

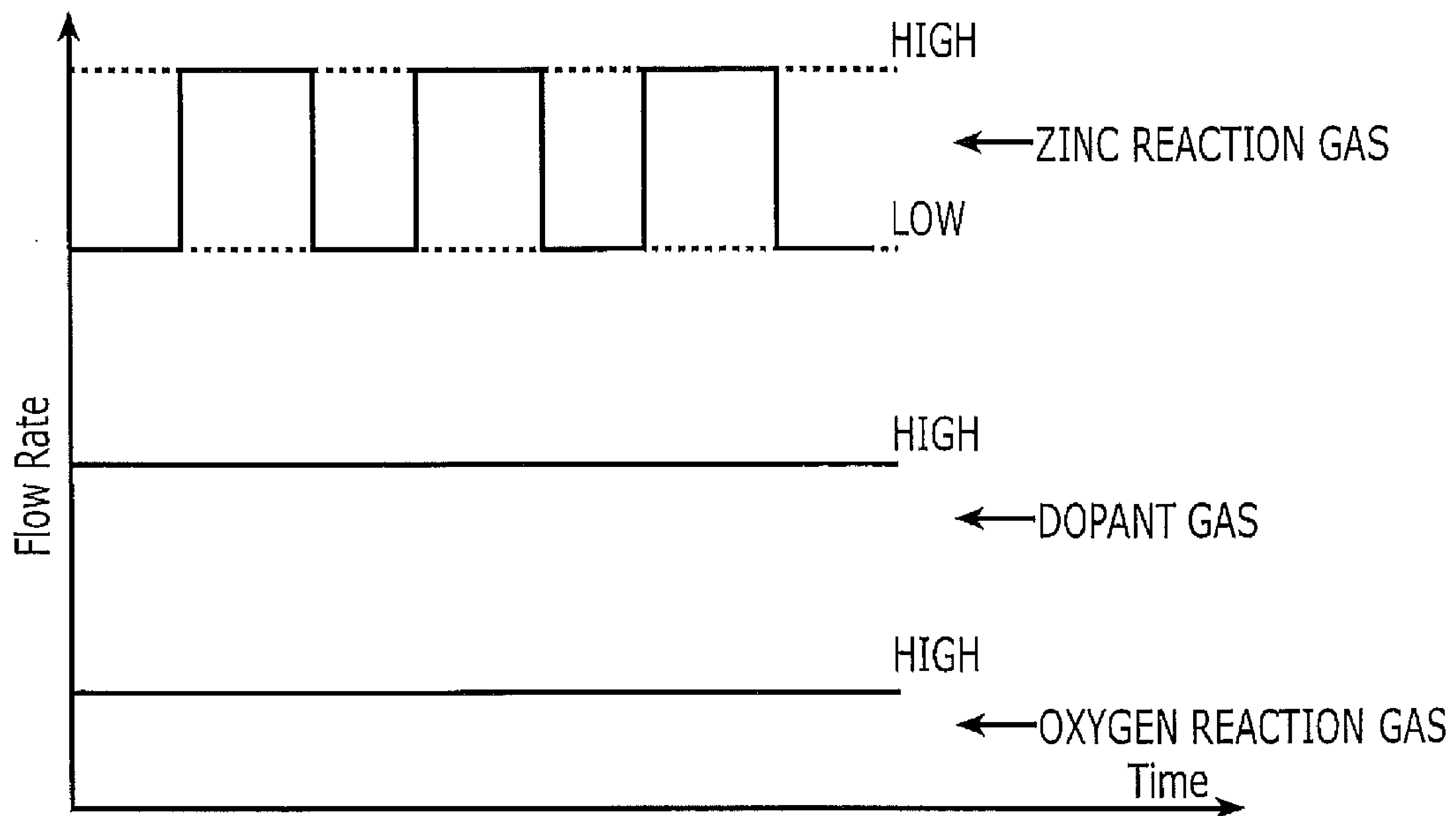

FIG. 1C

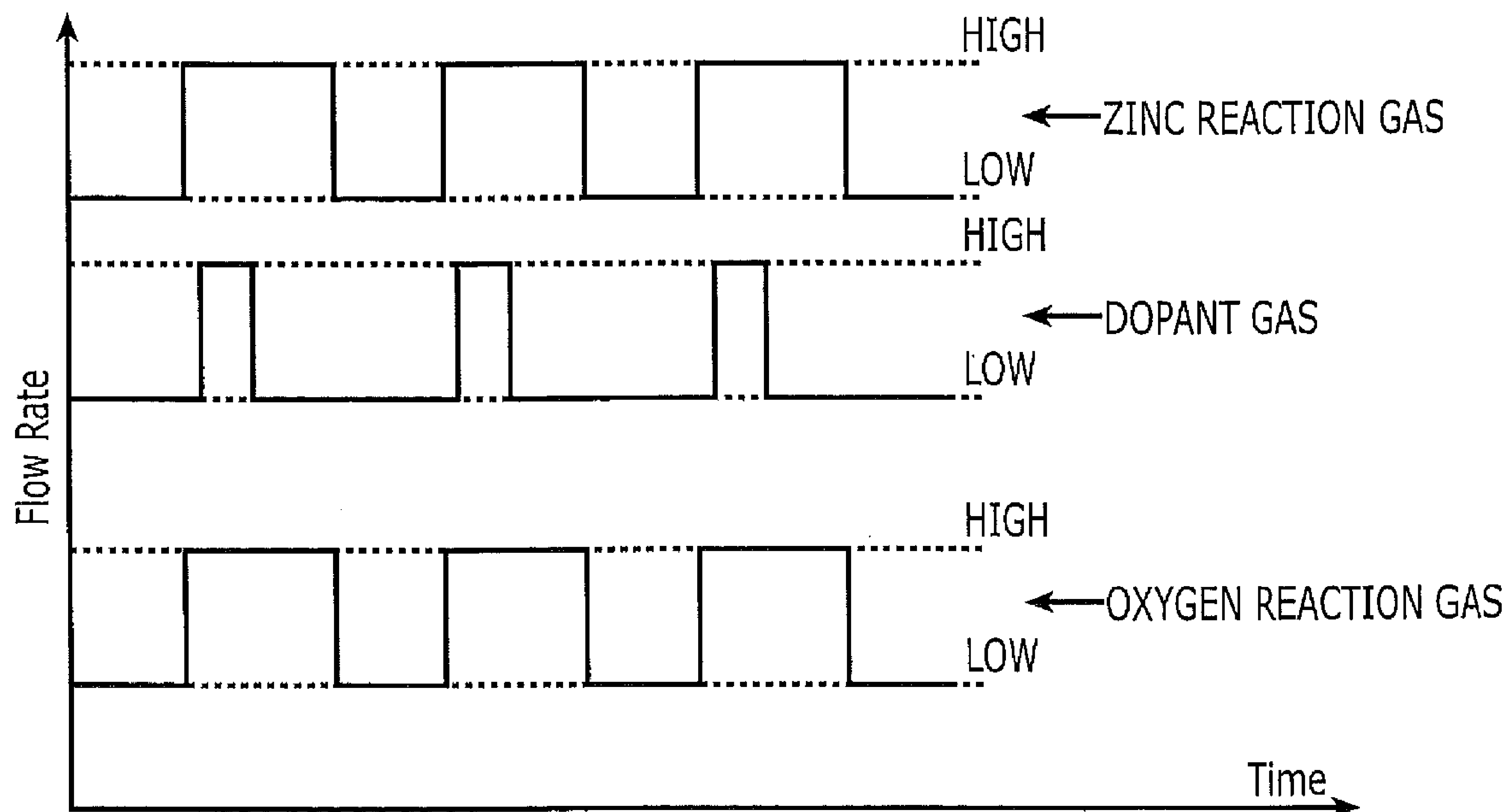

FIG. 1D

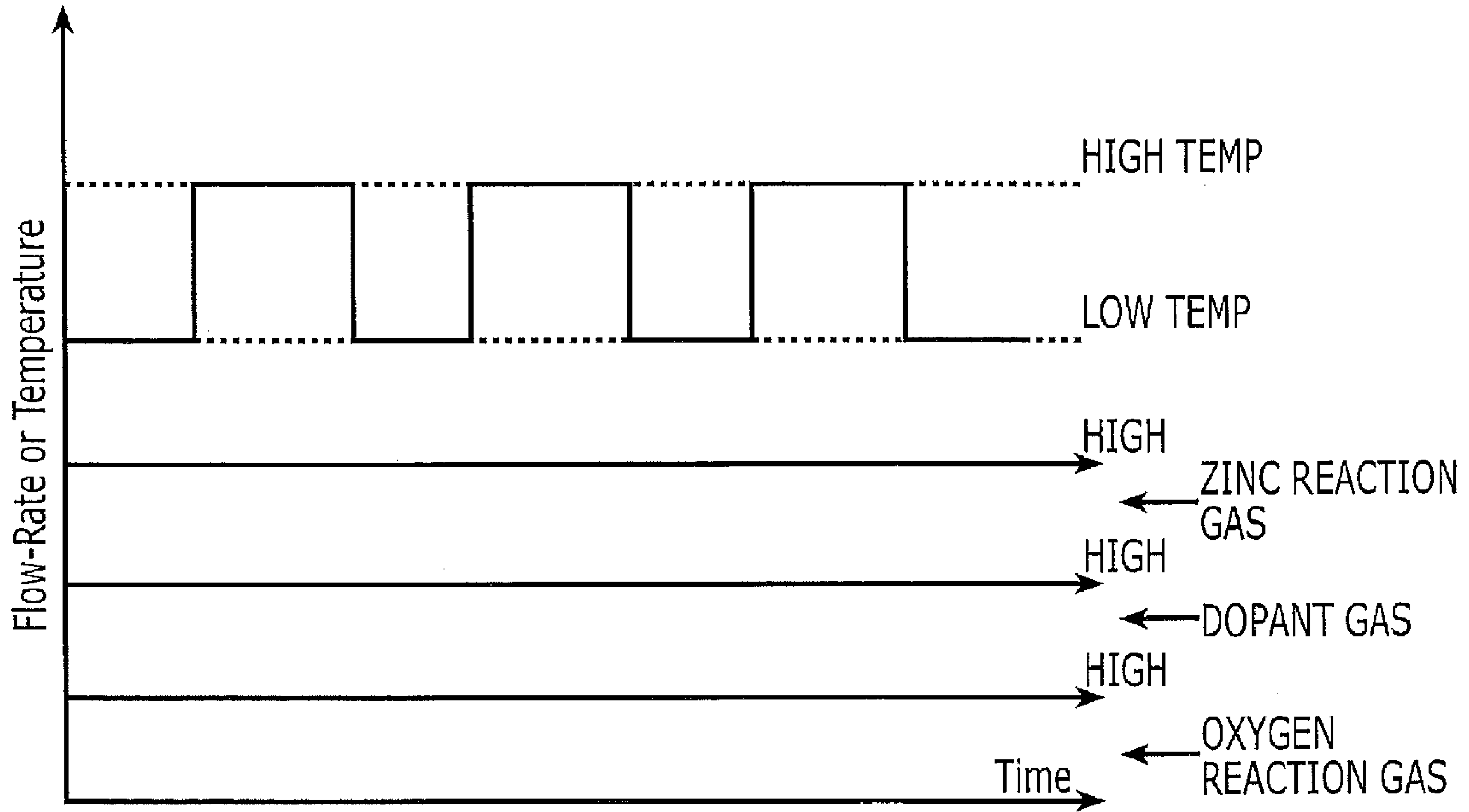

FIG. 1E

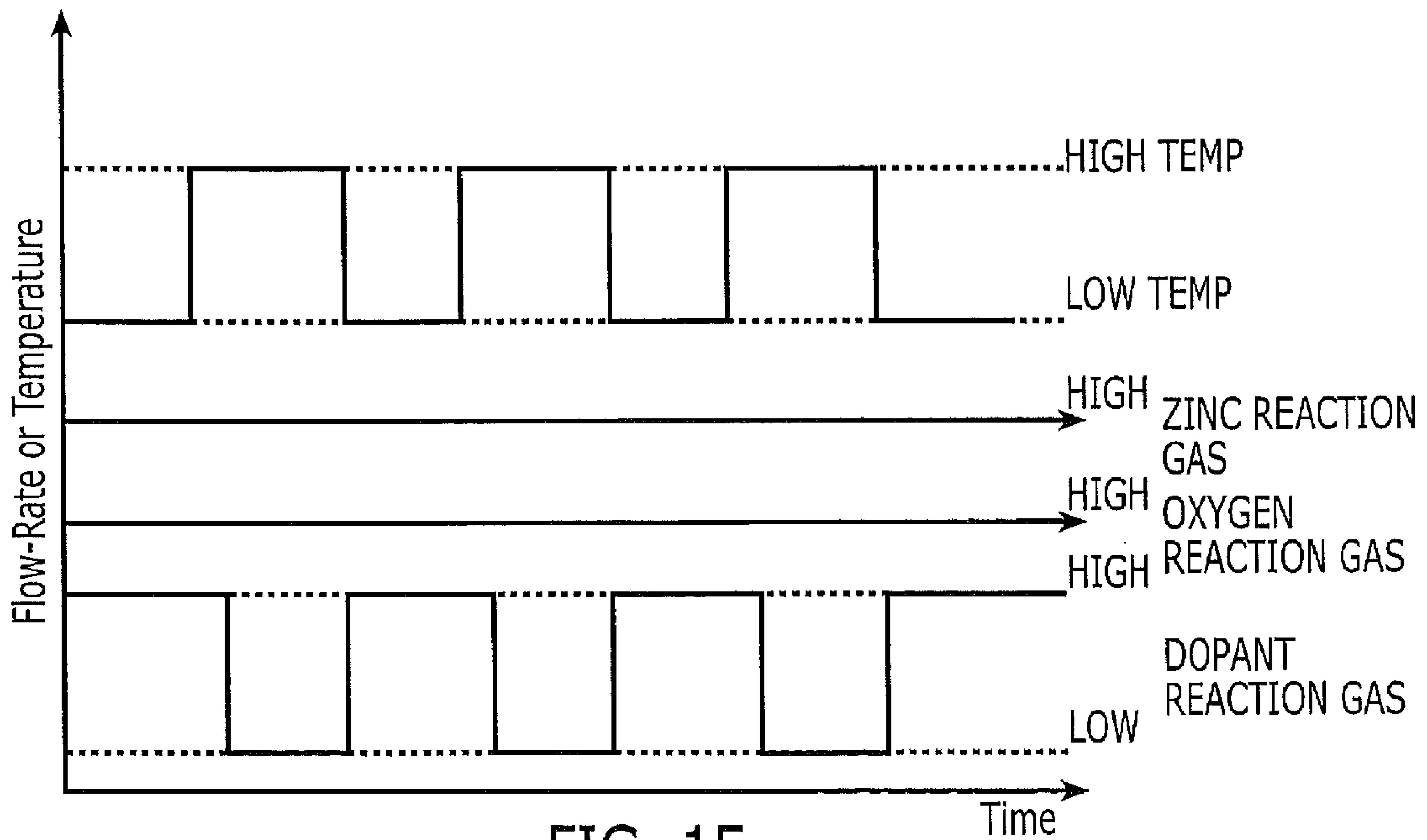

FIG. 1F

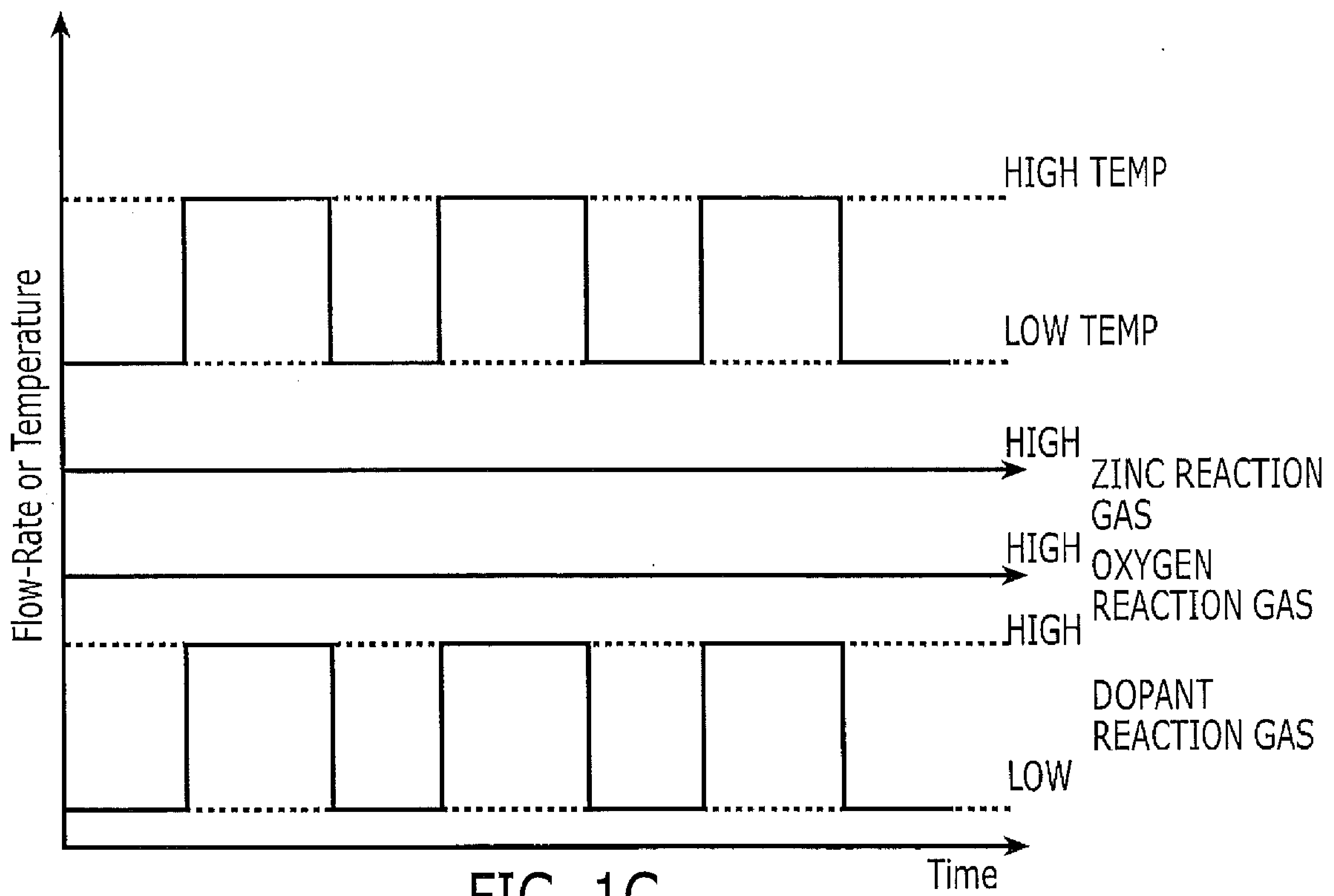

FIG. 1G

METHODS OF FORMING ZINC OXIDE BASED II-VI COMPOUND SEMICONDUCTOR LAYERS WITH SHALLOW ACCEPTOR CONDUCTIVITIES

REFERENCE TO PRIORITY APPLICATIONS

This application claims priority to U.S. application Ser. No. 11/551,058, filed Oct. 19, 2006, which claims priority to U.S. Provisional Application Ser. No. 60/728,352, filed Oct. 19, 2005, the disclosures of which are hereby incorporated herein by reference.

FIELD OF THE INVENTION

The present invention relates to semiconductor devices and methods of forming same and, more particularly, to compound semiconductor devices and methods of forming same.

BACKGROUND OF THE INVENTION

Zinc oxide (ZnO) materials typically have characteristics that are attractive for use in (i) optoelectronic semiconductor devices, which require emission or detection of electromagnetic radiation, (ii) high frequency and transparent transistors and (iii) radiation hardened devices, for example. However, the use of zinc oxide technologies has frequently been limited by a relative difficulty in reliably fabricating p-type zinc oxide materials with sufficiently high concentrations of relatively shallow acceptor impurities operating as p-type dopants.

Several attempts have been made to fabricate p-type zinc oxide materials using nitrogen (N) as a p-type dopant. Some of these attempts are disclosed in U.S. Patent Publication No. 2005/0170971 to Yata et al., entitled "P-type Zinc Oxide Semiconductor Film and Process for Preparation Thereof," and U.S. Pat. No. 6,908,782 to Yan et al., entitled "High Carrier Concentration P-type Transparent Conducting Oxide Films." Unfortunately, these attempts may result in zinc oxide films having only a relatively small percentage of activated p-type dopants at sufficiently shallow levels. Moreover, nitrogen may only have a limited solid solubility within zinc oxide, which operates as a limit on nitrogen activation and a limit on achieving uniform p-type dopant concentrations throughout a zinc oxide film.

Still further attempts have been made to incorporate phosphorus (P) and arsenic (As) as p-type dopants within zinc oxide films. Some of these attempts are disclosed in U.S. Patent Publication No. 2005/0285138 to Burgener et al., entitled "Persistent P-type Group II-VI Semiconductors," and U.S. Pat. No. 6,291,085 to White et al., entitled "Zinc Oxide Films Containing P-type Dopant and Process for Preparing Same." However, arsenic and phosphorus typically have poor acceptor ionization within zinc oxide, which may result from relatively high degrees of lattice relaxation at oxygen lattice sites. This relative high degree of relaxation typically causes these dopants to act as deep acceptors rather than shallow acceptors. Moreover, because acceptor conductivity within arsenic and/or phosphorus-doped zinc oxide devices may occur as a result of electrical coupling between these dopants and native point defects, which have concentrations that are highly dependent on temperature and variations in process conditions, these devices may be thermally unstable and have characteristics that cannot be reliably reproduced. To address these problems, post-growth annealing/activation steps have been considered to improve the electrical characteristics of the zinc oxide films. Such steps are disclosed in U.S. Pat. No. 6,852,623 to Park et al., entitled "Method for Manufacturing Zinc Oxide Semiconductors."

Zinc oxide films can be fabricated using conventional vapor phase epitaxy (VPE) techniques, which include molecular beam epitaxy (MBE) and metal organic vapor phase epitaxy (MOVPE), and chemical vapor deposition (CVD) techniques. As disclosed in U.S. Pat. No. 6,887,736 and U.S. Patent Publication No. 2005/0020035 to Nause et al., incorporation of acceptor dopants such as arsenic, phosphorous and nitrogen can also occur in-situ. Unfortunately, because arsenic, phosphorous and nitrogen have relatively limited thermodynamic solubility in zinc oxide, only relatively low levels of electrically active acceptor impurities can typically be obtained. Furthermore, not all elements from Groups IA, IB, VA and VB of the periodic table of the elements ionize as shallow acceptors in zinc oxide. For example, some Group IA elements such as sodium and cesium appear to ionize as donors, while other Group IA elements such as rubidium and francium do not appear to contribute electromigratable charge carriers. In addition, copper, which is a Group IB element, appears to ionize isoelectronically as a deep acceptor with localized holes that may not electromigrate or drift in the presence of an electric field as required in practical semiconductor devices. It also appears that possibly all Group VB elements, including vanadium, niobium and tantalum ionize as donors as well.

Zinc oxide films fabricated using conventional processing techniques, such as molecular beam epitaxy (MBE), vapor phase epitaxy (VPE) and metal organic vapor phase epitaxy (MOVPE) may also include crystals that are oxygen deficient resulting from the relatively low partial pressure of oxygen during fabrication. As will be understood by those skilled in the art, this oxygen deficiency may result in the compensation of introduced acceptor ions and thereby limit the concentration of p-type dopant species that contribute to conduction. Conventional MOVPE processing of zinc oxide may also be severely influenced by a relatively high degree of reactivity between oxygen and zinc atoms. This high degree of reactivity may result in the deposition of three dimensional crystals as opposed to more desirable two-dimensional crystals having characteristics that are more compatible with microelectronic devices. Accordingly, conventional MOVPE processing techniques may result in the fabrication of zinc oxide films having a high level of lattice dislocations and grain boundaries that impede device performance by operating as gettering cites for acceptors.

Additional attempts to achieve acceptor conductivities in zinc oxide also include co-doping with lithium ions to achieve highly compensated substrates and then introducing acceptor impurities as described in the aforementioned Yata et al. application, or co-doping with gallium and nitrogen impurities as described in U.S. Pat. No. 6,733,895 to Kadota et al. However, co-doping may be unsuitable for semiconductor fabrication processes because different diffusion mechanisms may exist for each acceptor impurity on the zinc and/or oxygen sublattice, which can lead to thermal instability of at least one of the impurities. For example, in the case of lithium introduced as a compensating impurity in p-type zinc oxide realized through the incorporation of nitrogen, the solubility of nitrogen is reduced as the concentration of lithium increases. This variation in solubility can lead to the dominance of lithium, which is a deep acceptor, on the electrical characteristics of the zinc oxide.

SUMMARY OF THE INVENTION

Methods of forming p-type ZnO-based II-VI compound semiconductor layers according to embodiments of the present invention include processing techniques that enable

incorporation of sufficient quantities of activated silver, potassium and/or gold dopants into a zinc sublattice within a ZnO-based II-VI compound semiconductor layer. These techniques use processing conditions that yield a net p-type dopant concentration of greater than about 1×10^{17} cm^{-3} therein, for dopants having an acceptor ionization energy below about 355 meV. The processing conditions may also yield a dopant activation level of greater than about 10% for the dopants having the desired acceptor ionization energy. The p-type ZnO-based II-VI compound semiconductor layer may be a layer selected from a group consisting of ZnO, ZnMgO, ZnCaO, ZnBeO, ZnSrO, ZnBaO, ZnCdO and ZnInO and MgCdZnO layers and composites of these layers.

In some of these embodiments, the process techniques for incorporating p-type dopants may include implanting the silver, potassium and/or gold dopants into the ZnO-based II-VI compound semiconductor layer at dose levels in a range from about 1×10^{13} cm^{-2} to about 1×10^{15} cm^{-2}. This implanting step may be performed as a single implanting step or as multiple implanting steps, which are performed at multiple different implant energy levels to thereby yield multiple implant peaks within the layer. An annealing step is then performed to more evenly distribute and activate the dopants and repair crystal damage within the layer. This annealing step may include annealing the ZnO-based II-VI compound semiconductor layer at a temperature in a range from about 250° C. to about 2000° C., in an ambient (e.g., chemically inert ambient) having a pressure in a range from about 25 mbar to about 7 kbar. More preferably, the annealing step may be performed at a temperature in a range from about 700° C. to about 900° C., in an oxygen ambient having a pressure of about 1 atmosphere.

According to additional embodiments of the present invention, the silver, potassium and/or gold dopants are incorporated into a zinc sublattice within a ZnO-based II-VI compound semiconductor layer using an metal organic vapor deposition technique. This technique may include exposing a substrate that is held at a temperature of greater that about 300° C. to a combination of a first reaction gas containing zinc, a second reaction gas containing oxygen and a dopant gas containing silver, potassium and/or gold dopants. This substrate may be selected from a group consisting of zinc oxide, III-nitrides, silicon, sapphire and/or glass.

Still further embodiments of the present invention include forming a ZnO-based II-VI compound semiconductor layer using an atomic layer deposition (ALD) technique. This deposition technique may include exposing a substrate to a combination of gases. This combination may include a first reaction gas containing zinc at a concentration that is repeatedly transitioned (e.g., pulsed) between at least two concentration levels during a processing time interval, a second reaction gas containing oxygen and a p-type dopant gas containing at least one p-type dopant species selected from a group consisting of silver, potassium and gold. According to additional aspects of these embodiments, a concentration of oxygen in the second reaction gas may be repeatedly transitioned (e.g., pulsed) between at least two concentration levels. In particular, a concentration of zinc in the first reaction gas and a concentration of oxygen in the second reaction gas may be transitioned in an alternating sequence, so that relatively high zinc concentrations in the first reaction gas overlap with relatively low oxygen concentrations in the second reaction gas and vice versa.

Moreover, according to still further aspects of these embodiments, a concentration of the at least one p-type dopant species in the p-type dopant gas may be repeatedly transitioned (e.g., pulsed) between at least two dopant concentration levels during the processing time interval. The pulses in the p-type dopant gas concentrations may have durations that are shorter than the pulses in the first reaction gas concentrations and also shorter than the pulses in the second reaction gas concentrations.

Methods of forming a ZnO-based II-VI compound semiconductor layer may also include using an iterative nucleation and growth technique. This technique may include using an alternating sequence of deposition/growth steps that favor c-plane growth (i.e., vertical growth direction, which causes nucleation) at relatively low temperatures interleaved with a-plane growth (i.e., horizontal growth direction, which causes densification) at relatively high temperatures to coalesce the layer. In particular, iterative nucleation and growth may include depositing a plurality of first ZnO-based II-VI compound semiconductor layers at a first temperature in a range from about 200° C. to about 600° C. and depositing a plurality of second ZnO-based II-VI compound semiconductor layers at a second higher temperature in a range from about 400° C. to about 900° C. These first and second ZnO-based II-VI compound semiconductor layers are deposited in an alternating sequence so that a composite layer is formed.

Still further methods of forming a p-type ZnO-based II-VI compound semiconductor layer include exposing the substrate to a combination of a first reaction gas containing zinc, a second reaction gas containing oxygen and a p-type dopant gas containing at least one p-type dopant species selected from a group consisting of silver, potassium and gold, while simultaneously transitioning a temperature of the substrate between at least two temperatures. These at least two temperatures may include a first lower temperature in a range from about 200° C. to about 600° C. and a second higher temperature in a range from about 400° C. to about 900° C. According to aspects of these embodiments, the concentration of the at least one p-type dopant species in the p-type dopant gas is repeatedly transitioned between at least two concentration levels while the temperature of the substrate is also being transitioned between the at least two temperatures. In particular, the concentration of the at least one p-type dopant species in the p-type dopant gas is transitioned in an alternating sequence relative to the transitioning of the temperature of the substrate so that relatively high concentrations of the p-type dopant species in the p-type dopant gas overlap with relatively low temperatures of the substrate and vice versa. Alternatively, the concentration of the at least one p-type dopant species in the p-type dopant gas is transitioned so that relatively high temperatures of the substrate overlap with a timing of relatively high concentrations of the p-type dopant species in the p-type dopant gas.

Methods of forming a p-type ZnO-based II-VI compound semiconductor region may also include incorporating sufficient quantities of silver, potassium and/or gold dopants into a zinc sublattice within the ZnO-based II-VI compound semiconductor region under processing conditions that yield a net p-type dopant concentration of greater than about 1×10^{17} cm^{-3} therein. In particular, a ZnO-based II-VI compound semiconductor layer may be formed on a substrate that is held at a temperature of greater than about 300° C., using a molecular beam epitaxy technique. This substrate may be selected from a group consisting of zinc oxide, III-nitrides, silicon, sapphire and/or glass, however, other substrates may also be used. In some of these embodiments, the molecular beam epitaxy technique may include Knudsen evaporation of a zinc source. Alternatively, the steps of forming a ZnO-based II-VI compound semiconductor layer may include using a chemical vapor transport technique. In this technique, hydride or halide transport of zinc to a substrate may be

provided. Still further embodiments may include using a physical vapor transport technique that includes transport of zinc to a substrate by evaporation, magnetron sputtering, flame hydrolysis deposition or sublimation. Liquid phase epitaxy techniques and solvus-thermal incorporation techniques may also be used to form the ZnO-based II-VI compound semiconductor region.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1**A is a flow diagram that illustrates methods of forming p-type ZnO-based II-VI compound semiconductor layers according to embodiments of the present invention.

FIGS. **1**B-**1**D are graphs that illustrate flow rate levels of reaction gases used to form compound semiconductor layers according to embodiments of the present invention.

FIGS. **1**E-**1**G are graphs that illustrate temperatures and flow rate levels of reaction gases used to form compound semiconductor layers according to embodiments of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention will now be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown. This invention may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

Referring now to FIG. **1**A, methods **10** of forming p-type ZnO-based II-VI compound semiconductor layers according to embodiments of the present invention may include placing a substrate in a semiconductor processing system (e.g., sealed processing chamber), Block **12**, and then heating the substrate to a desired temperature(s), Block **14**. This substrate may be selected from a group consisting of zinc oxide based II-VI compound semiconductor substrates, III-nitrides, silicon, sapphire and/or glass, however, other substrates may also be used. Thereafter, as illustrated by Block **16**, a zinc oxide based II-VI compound semiconductor layer is formed on the substrate by exposing a primary surface of the substrate to reaction and carrier gases. P-type dopants may be incorporated into the layer in-situ (i.e., while the layer is being formed) or after the layer is formed, Block **18**, to thereby yield zinc oxide based II-VI compound semiconductor layers according to embodiments of the present invention.

Some of the methods **10** of forming p-type ZnO-based II-VI compound semiconductor layer include processing techniques that enable incorporation of sufficient quantities of activated silver, potassium and/or gold dopants into a zinc sublattice within a ZnO-based II-VI compound semiconductor layer. These techniques use processing conditions that yield a net p-type dopant concentration of greater than about 1×10^{17} cm^{-3} therein, for dopants having an acceptor ionization energy below about 355 meV. The processing conditions may also yield a dopant activation level of greater than about 10% for the dopants having the desired acceptor ionization energy. Although not wishing to be bound by any theory, it is proposed that silver, potassium and gold impurities represent preferred dopants because they have ionization potentials that are about equal to or greater than the ionization potential of zinc atoms in the zinc sublattice and, therefore, do not cause significant lattice relaxation within the semiconductor layer being formed. These dopants also may be preferred because they can be processed to achieve relatively high levels of activation. This high degree of activation can be achieved, in part, because these dopants form a more covalent relationship with oxygen than the zinc-oxygen bond, which means their electron affinity is greater than the electron affinity of zinc. These dopants are also stable within the zinc sublattice, which means they do not contribute significantly to diffusion by interstitial transport mechanisms. The p-type ZnO-based II-VI compound semiconductor layer may be a layer selected from a group consisting of ZnO, ZnMgO, ZnCaO, ZnBeO, ZnSrO, ZnBaO, ZnCdO and ZnInO and MgCdZnO layers and composites of these layers.

Referring again to Blocks **16** and **18**, a p-type zinc oxide based II-VI compound semiconductor layer according to some embodiments of the invention may be initially formed on the substrate by exposing the substrate to reaction and carrier gases. P-type dopants may then be incorporated into the layer after the layer has been formed using ion implantation techniques. These techniques include implanting silver, potassium and/or gold dopants into the ZnO-based II-VI compound semiconductor layer at dose levels in a range from about 1×10^{13} cm^{-2} to about 1×10^{15} cm^{-2}. Dose levels significantly greater than about 1×10^{15} cm^{-2} may result in undesirable secondary phases and pronounced gettering of the implanted dopants. This implanting step may be performed as a single implanting step or as multiple implanting steps, which are performed at multiple different implant energy levels to thereby yield multiple implant peaks within the layer.

An annealing step is then performed to more evenly distribute and activate the dopants and repair crystal damage within the implanted layer. This annealing step may include annealing the ZnO-based II-VI compound semiconductor layer at a temperature(s) in a range from about 250° C. to about 2000° C., in an ambient (e.g., chemically inert ambient) having a pressure(s) in a range from about 25 mbar to about 7 kbar. This ambient may include the original reaction and carrier gases, oxygen, ozone, nitrogen, argon, or other chemically inert ambients, for example. More preferably, the annealing step may be performed at a temperature(s) in a range from about 700° C. to about 900° C., in an oxygen ambient having a pressure of about 1 atmosphere.

According to an additional embodiment of the present invention, the steps illustrated by Blocks **16** and **18** may be performed concurrently using an in-situ doping technique. In particular, the silver, potassium and/or gold dopants may be incorporated into a zinc sublattice within a ZnO-based II-VI compound semiconductor layer using an metal organic vapor phase epitaxy (MOVPE) technique. This technique includes transporting concentrations of an organometallic precursor of silver, potassium and/or gold by an inert gas (e.g., argon and/or nitrogen) to a gas stream containing an organometallic precursor of zinc and an oxygen source. This gas stream is directed towards a substrate that is held in an ambient at a growth temperature(s) between about 400° C. and about 1000° C. The pressure of the ambient is held in a range from about 20 Torr to about 76 Torr. This layer formation may be preceded by steps to nucleate ZnO-based II-VI compound semiconductor crystals on the substrate. This nucleation step may be performed for about 15 minutes while the substrate is held at a temperature of about 400° C. These crystals then undergo a densification process at 800° C. for about 15 minutes using an MOVPE technique with diethylzinc and oxygen as source gases. This densification process may be performed at pressures in a range from about 10 Torr to about 40 Torr.

Alternative oxygen source gases, including carbon dioxide, nitrous oxide, and/or nitrogen dioxide may also be used.

Another MOVPE technique includes halide-assisted MOVPE. This technique includes the use of a halide source of silver, potassium and/or gold dopants. These halide sources include silver, potassium and/or gold iodides and chlorides. The dopants are transported by an inert gas to a gas stream containing an organometallic precursor or halide source of zinc and an oxygen source, which is directed towards a substrate that is held in an ambient at a growth temperature(s) between about 400° C. and about 1000° C. The pressure of the ambient is held in a range from about 20 Torr to about 76 Torr. This layer formation may be preceded by steps to nucleate ZnO-based II-VI compound semiconductor crystals on the substrate. This nucleation step may be performed for about 15 minutes while the substrate is held at a temperature of about 400° C. These crystals then undergo a densification process at 800° C. for about 15 minutes using an MOVPE technique with $ZnCl_2$ and oxygen as source gases. This densification process may be performed at pressures in a range from about 10 Torr to about 40 Torr. Alternative oxygen source gases, including carbon dioxide and/or nitrous oxide, may also be used.

An additional MOVPE technique includes hydride-assisted MOVPE. This technique includes the use of a hydride source of silver, potassium or gold dopants. These dopants are transported by an inert gas to a gas stream containing an organometallic precursor or hydride source of zinc and an oxygen source, which is directed towards a substrate that is held in an ambient at a growth temperature(s) between about 400° C. and about 1000° C. The pressure of the ambient is held in a range from about 20 Torr to about 76 Torr. This layer formation may be preceded by steps to nucleate ZnO-based II-VI compound semiconductor crystals on the substrate. This nucleation step may be performed for about 15 minutes while the substrate is held at a temperature of about 400° C. These crystals then undergo a densification process at 800° C. for about 15 minutes using an MOVPE technique with ZnH_2 and oxygen as source gases. This densification process may be performed at pressures in a range from about 10 Torr to about 40 Torr. Alternative oxygen source gases, including carbon dioxide and/or nitrous oxide, may also be used.

Additional methods **10** of forming a p-type ZnO-based II-VI compound semiconductor layer may include using a molecular beam epitaxy technique. Using this technique, the source of silver, potassium and/or gold may be evaporated from a first Knudsen cell to a substrate concurrently with the evaporation of Zn from a second Knudsen cell in a partial pressure of oxygen. These steps may be performed at a growth temperature(s) of about 400° C. and a pressure(s) from about 25 mbar to about 700 mbar. Still further methods **10** may include using a physical vapor transport technique that includes transport of zinc to a substrate by evaporation, magnetron sputtering, flame hydrolysis deposition and/or sublimation.

Liquid phase epitaxy techniques and solvus-thermal incorporation techniques may also be used to form the ZnO-based II-VI compound semiconductor region. Moreover, a hydrothermal growth technique may be used that utilizes: (i) supercritical H_2O at between 34 bar and 4 kbar, (ii) a mineralizing agent such as LiOH and/or KOH, (iii) ZnO particles for nutrients, (iv) ZnO or GaN or sapphire templates for growth seeds and (v) an ore of silver, potassium and/or gold impurities. This ore may be obtained as an oxide, carbonate, sulphate, sulphide, halide, hydride and/or borate of these impurities. Preferred growth conditions include establishing dissolution and crystallization zones at 425° C. and 400° C., respectively, in a 5N LiOH/KOH buffer using an inert liner such as silver or platinum and water balancing and oxides of silver, potassium or gold at 28,000 psi or 1.9 kbar. The dopants can be interspersed with the nutrients or separately suspended and other sources of dopants that are miscible with water, such as hydrides, sulphates, borates, phosphates, and.or carbonates, can also be used.

Still further embodiments of the present invention include forming a ZnO-based II-VI compound semiconductor layer using an atomic layer deposition (ALD) technique. This deposition technique may include exposing a substrate to a combination of gases. As illustrated by FIG. **1**B, this combination may include: (i) a first reaction gas containing zinc at a concentration that is repeatedly transitioned (e.g., pulsed) between at least two concentration levels (high and low) during a processing time interval, (ii) a second reaction gas containing oxygen at a concentration that is repeatedly transitioned (e.g., pulsed) between at least two concentration levels (high and low), (iii) a p-type dopant gas containing at least one p-type dopant species selected from a group consisting of silver, potassium and gold, and (iv) an inert carrier gas (e.g., argon, nitrogen, . . .). In some of these embodiments, the low levels may be "off" levels and the high concentrations of the first and second reaction gases may be selected to achieve a Group VI/Group II ratio in a range from 1 to 500,000 and, more preferably, in a range from about 20 to about 200.

As illustrated by FIG. **1**B, the concentration of zinc in the first reaction gas and the concentration of oxygen in the second reaction gas may be transitioned in an alternating sequence, so that relatively high zinc concentrations in the first reaction gas overlap with relatively low oxygen concentrations in the second reaction gas and vice versa. Alternatively, as illustrated by FIG. **1**D, the concentration of zinc in the first reaction gas and the concentration of oxygen in the second reaction gas may be transitioned so that relatively high zinc concentrations in the first reaction gas overlap with relatively high oxygen concentrations in the second reaction gas. These transitions may be abrupt transitions or relatively gradual transitions.

FIG. **1**B also illustrates that a concentration of the at least one p-type dopant species in the p-type dopant gas may be repeatedly transitioned (e.g., pulsed) between at least two dopant concentration levels (high and low) during the processing time interval. These pulses have durations that are shorter than the pulses in the first reaction gas concentrations and also shorter than the pulses in the second reaction gas concentrations. Examples of dopant precursors include silver trifluoroacetate ($Ag(COOCF_3)$ and N,N-di(isopropyl)acetamidnate complexes of silver, for example.

Referring now to FIG. **1**C, an alternative ALD deposition technique may include exposing a substrate to: (i) a first reaction gas containing zinc at a concentration that is repeatedly transitioned between at least two concentration levels (high and low) during a processing time interval, (ii) a second reaction gas containing oxygen having a concentration that is held at a constant level, (iii) a p-type dopant gas having a concentration that is held at a constant level, and an inert carrier gas (e.g., argon, nitrogen, . . .).

Methods of forming a ZnO-based II-VI compound semiconductor layer may also include using an iterative nucleation and growth technique. This technique may include using an alternating sequence of deposition steps. In particular, iterative nucleation and growth may include depositing a plurality of first ZnO-based II-VI compound semiconductor layers at one or more first temperatures in a range from about 200° C. to about 600° C. and depositing a plurality of second ZnO-

based II-VI compound semiconductor layers at one or more second higher temperatures in a range from about 400° C. to about 900° C. These first and second ZnO-based II-VI compound semiconductor layers are deposited in an alternating sequence so that a composite layer is formed.

As illustrated by FIGS. **1**E-**1**G, still further methods of forming a p-type ZnO-based II-VI compound semiconductor layer include exposing the substrate to a combination of a first reaction gas containing zinc, a second reaction gas containing oxygen and a p-type dopant gas containing at least one p-type dopant species selected from a group consisting of silver, potassium and gold, while simultaneously transitioning a temperature of the substrate between at least two temperatures ("low" and "high"). These temperature transitions may be abrupt or gradual temperature transitions. In particular, these at least two temperatures may include a first lower temperature(s) in a range from about 200° C. to about 600° C. and a second higher temperature(s) in a range from about 400° C. to about 900° C. According to aspects of these embodiments, the concentration of the at least one p-type dopant species in the p-type dopant gas is repeatedly transitioned between at least two concentration levels while the temperature of the substrate is also being transitioned between the at least two temperatures. In particular, as illustrated by FIG. **1**F, the concentration of the at least one p-type dopant species in the p-type dopant gas is transitioned in an alternating sequence relative to the transitioning of the temperature of the substrate so that relatively high concentrations of the p-type dopant species in the p-type dopant gas overlap with relatively low temperatures of the substrate and vice versa. Alternatively, as illustrated by FIG. **1**G, the concentration of the at least one p-type dopant species in the p-type dopant gas is transitioned so that relatively high temperatures of the substrate overlap with a timing of relatively high concentrations of the p-type dopant species in the p-type dopant gas.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.

That which is claimed is:

1. A method of forming a p-type ZnO-based II-VI compound semiconductor layer, comprising:

depositing at least first and second p-type ZnO-based II-VI compound semiconductor layers on a substrate at a first temperature in a first range from about 200° C. to about 600° C. and at a different second temperature in a second range from about 400° C. to about 900° C., respectively.

2. The method of claim **1**, wherein said depositing comprises depositing the second p-type ZnO-based II-VI compound semiconductor layer on the first p-type ZnO-based II-VI compound semiconductor layer or vice versa.

3. The method of claim **2**, wherein said depositing comprises exposing the substrate to a combination of a first reaction gas containing zinc, a second reaction gas containing oxygen and a p-type dopant gas containing at least one p-type dopant species selected from a group consisting of silver, potassium and gold.

4. The method of claim **3**, wherein a concentration of the at least one p-type dopant species in the p-type dopant gas is repeatedly transitioned between at least two different concentration levels while a temperature of the substrate is being transitioned between at least two different temperatures.

5. The method of claim **3**, wherein a concentration of the at least one p-type dopant species in the p-type dopant gas is repeatedly transitioned between at least two different concentration levels while a temperature of the substrate is being transitioned between the first and second different temperatures.

6. A method of forming a p-type ZnO-based II-VI compound semiconductor layer, comprising:

providing a substrate; and

depositing a p-type ZnO-based II-VI compound semiconductor layer on the substrate using vapor phase epitaxy,

wherein the p-type ZnO-based II-VI compound semiconductor layer includes at least one p-type dopant species selected from a group consisting of silver, potassium and gold, and

wherein depositing the p-type ZnO-based II-VI compound semiconductor layer includes nucleating ZnO-based II-VI compound semiconductor crystals on the substrate.

7. The method of claim **6**, wherein depositing the p-type ZnO-based II-VI compound semiconductor layer is performed using metal organic vapor phase epitaxy.

8. The method of claim **6**, further comprising densifying the p-type ZnO-based II-VI compound crystals.

9. The method of claim **6**, wherein the at least one p-type dopant species is incorporated in-situ during vapor phase epitaxy.

10. The method of claim **6**, wherein nucleating the ZnO-based II-VI compound semiconductor crystals is performed at a temperature of about 400° C.

11. A method of forming a ZnO-based II-VI compound semiconductor layer, comprising:

depositing at least first and second ZnO-based II-VI compound semiconductor layers on a substrate at a first temperature in a first range from about 200° C. to about 600° C. and at a different second temperature in a second range from about 400° C. to about 900° C., respectively, said at least first and second ZnO-based II-VI compound semiconductor layers including at least one p-type ZnO-based II-VI compound semiconductor layer.

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